

Metallization of Fluid Hydrogen

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The electrical resistivity of liquid hydrogen has been measured at the high dynamic pressures, densities and temperatures that can be achieved with a reverberating shock wave. The resulting data are most naturally interpreted in terms of a continuous transition from a semiconducting to a metallic, largely diatomic fluid, the latter at 140 GPa, (ninefold compression) and 3000 K. While the fluid at these conditions resembles common liquid metals by the scale of its resistivity of 500 micro-ohm-cm, it differs by retaining a strong pairing character, and the precise mechanism by which a metallic state might be attained is still a matter of debate. Some evident possibilities include (i) physics of a largely one-body character, such as a band-overlap transition, (ii) physics of a strong-coupling or many-body character, such as a Mott-Hubbard transition, and (iii) processes in which structural changes are paramount.

I. INTRODUCTION

Hydrogen has been cited as the prototypical system for the study of the insulator-to-metal (IM) transition since Wigner and Huntington predicted in 1935 that the insulating molecular solid could transform to a conducting monatomic solid at sufficiently high pressure at 0K [1]. That is, although solid molecular hydrogen is a wide bandgap insulator ($E_g = 15$ eV) at ambient conditions, at sufficiently high pressure the insulating diatomic solid is expected to transform to a conducting monatomic solid or the electronic energy bandgap E_g of the diatomic solid is expected to close, resulting in an IM transition. Since Wigner and Huntington's paper, predictions of the transition pressure of the former has varied from 25 [1] to 2,000 GPa [2] at 0K. To date this transition in the solid at low temperatures has not been observed by optical measurements in the range 190 to 260 GPa. [3–5].

Metallization within the molecular solid phase by a band overlap mechanism is predicted to occur at pressures lower than is the case for the transition to the monatomic phase [6], but the transition pressure is structure-dependent [7–9], and the structure at densities close to metallization at 0 K is not known. Extrapolation of recent pressure-volume data up to 120 GPa in the hcp phase yields a predicted dissociative transition of 620 GPa [10]. Both the monatomic and diatomic metallic solids have been predicted to be high-temperature superconductors [11,12].

Electrical conductivity measurements indicate that hydrogen becomes metallic (i.e. conducting [13]) at 140 GPa, ninefold compression of initial liquid density, and 3000 K [14]. Metallization is expected when pressure and density are sufficiently high that the electronic bandgap decreases from the value at ambient conditions of 15 eV down to ~ 0.25 eV, the temperature of these experiments. Extrapolation by means of the Simon equation of the melting curve of H_2 measured at low pressures [15] gives a melting temperature of 1800 K at 140 GPa. Thus, as stated, metallization probably occurs in the high temperature fluid.

Electrical conductivity has also been measured under single-shock compressions up to 20 GPa and 4600 K [16]. Those measurements showed that electronic conduction is thermally activated in the semiconducting fluid. Electrical conductivity experiments using explosively driven magnetic flux compression to isentropically compress liquid hydrogen have shown that the conductivity becomes greater than $1(\Omega cm)^{-1}$ at 200 GPa and 400 K [17]. Although this conductivity does not conform to metallic values, this experiment demonstrates that the electrical conductivity increases at high pressure and temperature. Shock Hugoniot and temperature data have also been measured [18–20].

Hydrogen is important for astronomy because its cosmological abundance is about 90 atomic percent, and the understanding of dense hydrogen is particularly important to planetary science. Jupiter and Saturn contain over 400 Earth masses, most of which is fluid hydrogen. Jupiter-size planets now being discovered close to nearby stars [21] probably contain massive amounts of hydrogen as well, and the interiors of these giant planets are likely to be at high pressures and high temperatures and in the fluid state [22]. Because of the large mass diffusion coefficient and low thermal conductivity [23], magnetic fields are produced by the convective motion of electrically conducting fluid hydrogen by dynamo action [24]. Implications for Jupiter of recent measurements on dense hydrogen at high pressures and temperatures have been described elsewhere [25].

Because of the high kinetic energy in the impactor (0.5 MJ), in a sense we are actually working at a confluence of High Energy and Condensed Matter Physics. This energy is comparable to the total kinetic energy of all the protons and antiprotons in the beams in the Tevatron at the Fermi National Accelerator Laboratory. Here energy enables discovery of novel states of condensed matter, analogous to the discovery of novel states of subnuclear matter.

II. FINITE TEMPERATURES

The distinguishing feature of these experiments is achievement of a stable hydrogen sample at 3000 K and 100 GPa pressures. It is desirable to look for the IM transition at higher temperatures because phenomena which inhibit metallization in the dense solid; namely, crystalline and orientational phase transitions [26,27], do not occur in the disordered fluid. However, because of the large mass-diffusion coefficient and chemical reactivity of hydrogen at high temperatures, it is essential to use a temperature pulse. The duration of this pulse should be sufficiently long to achieve equilibrium and sufficiently short that the sample cannot diffuse away nor react chemically before the experiment is completed. The ~ 100 ns duration of shock compression satisfies these criteria. Our temperature (equivalent to 0.3 eV) is relatively low for the electron distribution being probed because the energy gap at ambient pressure is 15 eV and the zero point energy of the molecule is 0.3 eV.

III. EXPERIMENT

Conditions of high pressures, densities, and temperatures were produced by impact of a planar metal plate onto a cryostat containing liquid hydrogen. A two-stage light-gas gun was used to accelerate the impactor plate up to $\sim 7\text{ km/s}$ [28]. Hydrogen gas is used to accelerate the projectile because it has the highest sound speed of any gas and thus produces the highest impact velocity and pressure. The magnitude of the pressure generated by the impact is determined by the impact velocity [29] and the Hugoniot equations of state of impactor and target [30,31]. To achieve highest densities and lowest temperatures at high pressures, the sample must have a relatively high initial density. High densities were achieved by using a liquid sample at 20 K. [18,32]. We applied our previous techniques to measure electrical conductivities [16,33] to the configuration illustrated in Fig. (1).

The sample is 0.5 mm thick and 25 mm in diameter contained between two electrically insulating sapphire (single-crystal z-cut Al_2O_3) anvils, 2.0 mm thick and 25 mm in diameter. These are contained between two 2.0 mm-thick Al disks. Al is strong, ductile, and a good thermal conductor at 20 K, which facilitates condensing the sample from high-purity gas. Both H_2 and D_2 samples were used, depending on the final density and temperature desired. At the relatively high final temperatures achieved ($\sim 3000\text{ K}$), possible effects of different zero-point energies for hydrogen and deuterium are negligible. Stainless steel electrodes exit the sample holder to the right. In the metallic phase four electrodes are used; two outer electrodes for current and two inner electrodes to measure potential difference. Two electrodes are used if hydrogen is in a state of poor conductivity. The electrical circuit for four-probe measurements is shown in Fig. (1b). Shock compression switches the hydrogen sample into the circuit when its conductivity becomes significant. Voltages were measured differentially with 1-ns time resolution. Current was measured with a Rowgowski coil. Typical currents were $\sim 1\text{ A}$ and voltages were a few tens of mV. The resistance R is directly proportional to the resistivity ρ , so that $R = C\rho$. To determine the cell constant C , steady-state, three-dimensional current flow simulations were performed to calculate R and ρ [14].

IV. THERMODYNAMIC STATES

This experiment achieves highly condensed matter relatively close to the 0 K isotherm by means of a reverberating shock [34]. The impact generates an initial pressure P_f in the Al_2O_3 . When this shock reaches the liquid hydrogen, the pressure of the shock drops until the release pressure of sapphire matches the Hugoniot of liquid hydrogen. This drop is about a factor of 30 in pressure. The shock in hydrogen then reverberates back and forth between the sapphire anvils until the pressure reaches P_f , the pressure incident initially from the sapphire. Thus, the first wave in hydrogen is a weak shock and the total of the successive shock reverberations is a quasi-isentrope. This fast compression is near adiabatic and the temperature of hydrogen rises. This process causes a final temperature which is about an order of magnitude smaller than would be achieved by a single shock to the same final pressure.

The initial weak shock occurs in $< 10^{-12}\text{ s}$ (Fig.(2a)); the following quasi-isentrope takes $\sim 5 \times 10^{-8}\text{ s}$. The corresponding effect on the thermodynamics is illustrated in Fig.(2b). These various pressure-density states were calculated using the equation of state of Kerley [35]. Shock reverberation is necessary to reach metallization near 0.7 g/cm^3 .

The densities and temperatures must be known to analyze the electrical conductivities. At present no means to measure them exist; they must be calculated. The densities and temperatures were calculated with two equations of state for hydrogen. One was developed by Kerley [35] before recent shock data were available; it neglects molecular dissociation at the conditions in our experiments. The other is due to Ross, which is based on our recent shock temperature data and includes molecular dissociation [19]. The preferred values were those calculated with Ross' model, because it is based on recent data. The calculated final pressures in the hydrogen or deuterium agree to within 1% with the initial shock pressures in the sapphire calculated by shock impedance matching. Based on these calculations, the systematic uncertainties in calculated density and temperature are 5% and 20%, respectively.

V. ANALYSIS OF CONDUCTIVITY DATA

The experimental resistivity data are plotted as $\log(\rho)$ versus pressure in Fig. (3). The change in slope at 140 GPa is indicative of the transition to the metallic state. We analyzed results in the semiconducting range, 93-135 GPa, by fitting the data to the dependence of conductivity for a thermally activated semiconductor:

$$\sigma = \sigma_0 \exp(-E_g(D)/2k_B T), \quad (1)$$

where σ is electrical conductivity, σ_0 depends on density D and relatively weakly on T , $E_g(D)$ is the density-dependent mobility gap in the electronic density of states of the fluid, k_B is Boltzmann's constant, and T is temperature.

Seven data points with error bars of 20 to 50% were fit to Eq. (1), the results being: $E_g(D) = 1.12 - (54.7)(D - 0.30)$, where $E_g(D)$ is in eV, D is in mol/cm^3 ($0.29 - 0.32 \text{ mol}/\text{cm}^3$), and $\sigma_0 = 66 (\Omega\text{cm})^{-1}$. Similar results are obtained using densities and temperatures calculated with Kerley's model [14]. $\sigma_0 = 200 - 300 (\Omega\text{cm})^{-1}$ is typical of liquid semiconductors [36]. Since σ_0 is within a factor of 3 of the typical value, this result is reasonable. The theoretical rate of bandgap closure near metallization at 0 K of molecularly disordered hcp hydrogen is $40\text{eV}/(\text{mol}/\text{cm}^3)$ [9], which is comparable to our value of $\sim 60\text{eV}/(\text{mol}/\text{cm}^3)$ obtained by fitting. Thus, this slope is also comparable to what is expected. From our fit the gap $E_g(D)$ and k_BT are equal at a density of $0.32 \text{ mol}/\text{cm}^3$ and a temperature of $\sim 2600\text{K}$ (0.22eV). In this region the energy gap is smeared out thermally, activation of electron carriers is complete, disorder is saturated in the fluid, and conductivity is expected to be weakly sensitive to further increases in pressure and temperature, provided the fluid does not change significantly. At $0.32 \text{ mol}/\text{cm}^3$ the pressure is 120 GPa, which is close to the 140 GPa pressure at which the slope changes in the electrical resistivity (Fig. (3)).

At pressures of 140 to 180 GPa the resistivity changes character; it is essentially constant at $500\mu\Omega\text{cm}$, equivalent to a conductivity of $2000(\Omega\text{cm})^{-1}$. This value is typical of the fluid (monatomic) alkali metals Cs and Rb at 2000 K undergoing the same transition [37]. Also, the minimum electrical conductivity of a metal is given by $\sigma = 2\pi e^2/3\hbar a$, where e is the charge of an electron, \hbar is Planck's constant, and a is the average distance between particles [38]. In this case $a \sim D_m^{-1/3}$, where D_m is the density of hydrogen at metallization. The calculated minimum metallic conductivity is $4000(\Omega\text{cm})^{-1}$, which is in good agreement with the experimental value of $2000(\Omega\text{cm})^{-1}$. Thus, fluid hydrogen becomes conducting at about 140 GPa and 3000 K via a continuous transition from a semiconducting to metallic fluid, in which the electronic activation energy is reduced by pressure to k_BT .

An important point to keep in mind in what follows is this; though the characteristic time of the experiments are probably long enough to achieve equilibrium in a single phase, it is possible that the system has not reached its equilibrium phase should it happen that the system has just crossed a phase boundary.

VI. THEORETICAL CONSIDERATIONS

In hydrogen, at the conditions of the experiment, the confluence of thermal and quantum effects link the physics of dissociation and metallization, electronic and atomic ordering, and ionization and chemical (cluster) formation. Together these can lead to a remarkably rich phase diagram, most of which remains unexplored. The metallization experiment [14] reveals a new section of this phase diagram, and gives hints to its further structure, as shown in Fig. (4). Traditionally, theoretical interest has focussed on the change from a diatomic to a monatomic liquid or plasma, as well as the change from a metal to an insulator. In the new experimental regime now opened up, translational energies appear to match the vibron energies, and as such the metallization experiment may be probing both types of changes. With these confluences in mind we comment in turn on some interesting theoretical questions raised by the experiment, namely: (a) Why does the resistivity, the primary measured quantity, take the value it does?, (b) Why does the metal-insulator transition occur at a considerably lower pressure in the liquid than is predicted in the solid?, (c) What is the detailed mechanism of the metal-insulator transition?, and (d) What further experimental probes might clarify the situation?

VII. THE SCALE OF RESISTIVITY IN LIQUID METALLIC HYDROGEN

The fundamental approach to the transport properties of liquid metals is via the Kubo-Peierls-Greenwood theory, based on linear response of the system to a weak external field $E(t)$. The static conductivity $\sigma(0)$ is then given by:

$$\sigma(0) \sim \int_0^\infty \langle j(0)j(t) \rangle dt \quad (2)$$

where $\langle j(0)j(t) \rangle$ is a current-current correlation function for the many-electron system. If the self-energy of the electron system is sufficiently small (from all sources of interaction) then an expansion in the self-energy leads to an inversion of σ for the resistivity, and at lowest order this is equivalent to first-Born approximation within the Boltzmann semi-classical approach to transport. In the high temperature limit it leads to the well known Ziman formalism [39–41] for degenerate electron systems, and this has been remarkably successful at predicting the resistivity of liquid metals to within about a factor of two, as well as trends seen in alloys, thermopower and the temperature dependence of the resistivity [42]. It requires as input the static structure factor $S(q)$ of the scattering system, an electron-ion-interaction, and the assumption of an appropriate high temperature limit.

To assess the applicability of this approach to the present problem, we may consider the case of liquid Si and Ge which prior to melting are not metals, though conduction by thermally excited carriers is evident. As fluids they are significantly under-coordinated ($\sim 5-6$) which reflects persistent covalent effects and hence interactions going beyond the pair model. In applications of the Ziman formalism to this problem, the tangible effects of remnant covalency are included only through the static structure factor $S(q)$; 4 electrons per ion are usually assigned to the conduction process [but see below].

In some ways, the situation for hydrogen can be considered physically similar to Si or Ge, only more extreme. It is, again, a fundamentally covalent (but not necessarily a network) system, and structurally it cannot be described just in terms of pairwise proton-proton interactions. The viewpoint taken from liquid Si (a metal) can be taken here if the state possesses a Fermi surface: in the application of the weak scattering formalisms covalency manifests primarily through $S(q)$ and in the specification of the fundamental excitations associated with the structure. As a first approximation (compare with the case for Si), two electrons per “molecule” could be taken to participate in conduction, but with a significant density of states correction to be applied later. Given this fundamental picture essentially tied to the pairing picture of the solid, we proceed to investigate the resistivity of liquid metallic *molecular* H_2 (in the experimental metallization regime) starting with the Ziman expression [39–41]. We express the resistivity ρ_L originating with a given type of carrier as:

$$\rho_L = \frac{m}{n_c e^2 \tau}, \quad (3)$$

where m is the carrier mass, n_c is the carrier density, and τ is a measure of the relaxation time. In its simplest form the Ziman formalism gives [43]:

$$\rho_L = \left(\frac{a_0 \hbar}{e^2} \right) \frac{6\pi}{(n_s)(k_F)^2} \int_0^1 S(y) |v(y)|^2 (y)^3 dy, \quad (4)$$

where $y = q/2k_F$ is the wave vector scaled by twice the Fermi wave-vector, n_s the number density of scatterers, $v(y)$ the screened coulomb potential, $S(y)$ the structure factor describing the proton-proton density fluctuations which scatter the carriers, and $(a_0 \hbar/e^2)$ can be viewed as the atomic unit of resistivity (it has the value of $21.7 \mu\Omega cm$).

The structural average required in the static structure factor appearing in (4) is not simple given the conditions of the experiment. In the first place translational energies appear well matched to rotational energies, and also to vibron energies. The kinematic transfer of energy from translational to vibrational degrees of freedom will be competitive with transference of translational energy to rotational energies. Accordingly, for this system the temperature and the density conspire in such a way that a standard averaging over rotational degrees of freedom prior to translational averaging is not secure. Secondly, orientational and translational entanglement leads to considerable self-averaging in the determination of the static structure factor. Thirdly, it has to be emphasized that so far as the vibron excitations are concerned, the system is not at high temperatures, which affects both structural [44] and scattering [45] physics.

In a naive approach using the usual free-electron density of states, and with the approximations introduced above for the structure factor $S(q)$, a resistivity of about $50 \mu\Omega cm$ is found from (4), a significantly larger figure than obtained in previous calculations of monatomic H [46], but still considerably lower than the $500 \mu\Omega cm$ measured experimentally [14]. However, this is to be expected since in the one-electron picture we also anticipate a significant decline in the density of states at the Fermi energy [47].

If the band-gap has only just closed we expect a lowering of the density of states as compared with the full free-electron case which in turn can be linked to a significantly reduced effective carrier density. Equation (3) shows that a reduced number of carriers raises the resistivity [48]; we also expect related multiple-scattering and other strong-coupling effects [49] to be relatively important in this regime, and these effects also lead to higher resistivities. Thus by taking into account physics beyond the usual one-band picture our result of $\sim 50 \mu\Omega cm$ can only be seen as something of a lower bound. Since the overlap and related electron density is expected to increase with increasing density, this modified Ziman picture predicts that the resistivity at fixed temperature should continue to fall with increasing pressure so long as the liquid maintains its pairing correlations. We emphasize, however, that the pairs are in no sense permanent (again an analogy to fast exchange in liquid Si can be made) although they are long-lived on *electronic* timescales and as such influence the electronic structure.

At present the experimental results have large error bars (20% in the metallic state) and are in too small a pressure range to confirm or falsify any predicted pressure dependence of the resistivity, but the actual value of the resistivity near metallization seems consistent with this picture, though this is not the only possible interpretation (see below).

VIII. THE ONSET OF THE INSULATOR TO METAL TRANSITION

At first sight the lower pressure and density of the metal-insulator transition in the liquid compared to the solid may seem surprising. One would expect the greater disorder (as compared with the solid) to delay the closing of the gap and the subsequent onset of metallization as is for example the case in Hg, another divalent pressure-induced metal-insulator transition [50]. However, a closer look at the origin of the bandgap in the solid phase reveals a more complex possibility which can be illustrated in the Pa3 structure, an isotropic solid which best mimics the high coordination and orientational averaging characteristics of the “paired” liquid. The lower bands in such a structure can be represented by an equivalent face-centered cubic description [51] where the principal Fourier components of the electron interaction with pairs are given by

$$V_{111} = (3/4\pi r_s^3 a_0^3) S_0(111) v(111) \quad (5)$$

and

$$V_{200} = (3/4\pi r_s^3 a_0^3) S_0(200) v(200). \quad (6)$$

Here S_0 is the structure factor per proton, and is given by

$$\begin{aligned} S_0(l, m, n) = \frac{1}{4} \{ & \cos 2\pi\alpha(l + m + n) + (-1)^{m+n} \cos 2\pi\alpha(l - m + n) \\ & + (-1)^{l+m} \cos 2\pi\alpha(-l + m + n) \\ & + (-1)^{n+l} \cos 2\pi\alpha(l + m - n) \} \end{aligned} \quad (7)$$

with $\alpha = d(r_s)/\sqrt{3}a$ ($2a$ being the separation, on average, between protons), and $v(K)$ is the Fourier transform for the screened potential of a single proton.

Increase of the temperature to ($k_B T \sim \hbar\omega_{vib}$) significantly excites the pairs into higher anharmonic vibrational states resulting in large amplitude spatial fluctuations. These in turn will lower the gap by a corresponding Debye-Waller factor, and given that the excursions are appreciable, the lowering can be significant. This can be demonstrated most easily by extending one of the 4 pairs in the Pa3 structure to a separation of $2d'$ ($2d' > 2d$) while the other basis pairs are kept fixed. From (7) the structure factor per proton for such a separation becomes

$$S(l, m, n) = S_0(l, m, n) - \frac{1}{2} \sin[\pi(\alpha' - \alpha)(l + m + n)] \sin[\pi(\alpha + \alpha')(l + m + n)], \quad (8)$$

which shows immediately that the gap will be reduced when the pair extends. This gives a strong hint of the likely effect of temperature, primarily to reduce the gap, and to promote an earlier transition from insulator (or semi-conductor) to metal. Note that a displacement arising with acoustic phonons can also contribute to this effect.

IX. THE PHYSICAL CHARACTERISTICS OF THE INSULATOR -METAL TRANSITION

At the one-body level the general closing of the gap with increasing pressure and density appears well established, but what exactly happens upon close approach to the metal-insulator transition in hydrogen? Some possibilities now follow:

A. Scenario 1: Metal-insulator transition induced by one-body physics

In a continuous single particle approach, the gap closes and progressively more and more carriers are excited into the conduction band; structurally this implies strong pairing correlations. Depending on the decline of this gap, the emerging conductivity can be significant. Experiments and theory converge on a consistent picture for hydrogen where the band-gap decreases with increasing pressure, both in the solid [9,52] and liquid [16] phases. In the solid, the concept of an indirect gap closing with increase of density in the paired phase is robust when calculated in various crystal structures and it also obtains under orientational disorder [6,8,9]; if generalized to the separation between mobility edges [53], we expect it to carry through for the liquid phase as well [54]. Accordingly, under the assumption that the liquid remains largely paired, this view leads to a picture where the one-electron physics of the liquid may be similar to that of the solid; under pressure mobility edges are gradually approaching, and if this continues hydrogen

will be transformed from a liquid semi-conductor to a liquid semi-metal. As pressure increases further the “bands” overlap (mobility edges cross), and the effective carrier density continues to increase, eventually becoming degenerate [55].

The vibrational dynamics of the H_2 molecules imply an interesting possibility for the scale of conductivity in the semi-metallic regime (i.e. $k_B T \sim E_g$). If we assume that the electrons hop from pair to pair when close approach sufficiently increases orbital overlap, then their time-scale will be set by those translational excursions which bring molecules into sufficient proximity that wave-function overlap is especially effective (i.e. $\tau \sim 10^{-14}$ s). Together with a standard semi-conductor picture invoked to estimate the carrier density (see e.g. p 575 of [56]), this quickly leads to resistivities as low as $\sim 700 \mu\Omega cm$ for $E_g \sim 2k_B T$ [43]!

Note, however, that the liquid phase corresponds to proton arrangements that are strongly disordered. If viewed at low temperatures, disorder can lead to states that lack diffusion, via Anderson-localization. The role of temperature is then to excite electrons from such states. Note however, that the condition for Anderson localization is similar to the condition for the Mott transition:

$$D_m^{1/3} a^* \sim C, \quad (9)$$

where a^* is a measure of the localized orbital size, and C is typically about 0.3 [53]. Under the assumption that the Bohr radius for diatomic hydrogen is roughly the same as the Bohr radius of monatomic hydrogen, $D_m^{1/3} a^* \sim 0.3$ at experimental metallization conditions.

B. Scenario 2: Metal-insulator transition and the role of many-body physics

Mott [53] argued that a gap will never close continuously because upon restoration of residual many-body interactions, the formation of excitons which subsequently unbind upon further closing of the gap will lead to a jump in the conductivity. We expect in this case that the temperature of ~ 0.3 eV will be too high for the formation of excitons [57] but this does not rule out some other type of correlation driven transition near band-gap closure. For example, the Hubbard U for monatomic hydrogen is about 17 eV [53] while the free-electron band-width at experimental conditions is around 20 eV, which is probably an upper bound. Since the effects of disorder and correlation are expected to reinforce each other [58] the possibility of conductivity by thermal excitation across a declining Mott-Hubbard gap emerges. If we are in the regime where electron-electron interactions play an important role, the effect of spin becomes non-trivial. The twin effects of strong correlation and disorder as they influence the metal-insulator transition are not completely understood; they combine with some force in the hydrogen problem.

The highly successful semi-empirical Herzfeld polarization catastrophe criterion predicts that H_2 will become metallic only upon about ~ 11 fold compression [59] (generally for ordered phases). However, we note that there is some ambiguity in the definition of the various quantities entering these criteria (for instance the meaning of local polarizability in the present environment), a problem that becomes even more acute for hydrogen where the fluid phase is involved.

C. Scenario 3: Metal-insulator transition induced by structural change

If simple pressure induced band-gap closure in the paired state is preceded by significant structural change, metallization can also precede complete closure of this gap. Perhaps the best known case of a metal-insulator transition driven by structural change is the metallic behavior seen when melting the elemental semi-conductors such as Si and Ge (as discussed above). The change in band-structure is driven by the change in local atomic structure, in this case a relatively small increase in coordination. In the case of hydrogen, structural change associated with, for example the rapid decline of pairing correlation, is a likely candidate. In the liquid phase, we have a direct parallel of the crystalline case discussed in section VIII. above.

In fact, the Wigner-Huntington proposal [1] itself falls into the class of MI transitions induced by structural changes. Here it was predicted that increasing pressure (at $T=0$) could lead to dissociation in hydrogen, resulting in a structure with one electron per unit cell and concomitant metallic behavior for paramagnetic states [60]. Even at relatively low densities, increasing the temperature to regimes comparable with the dissociation energy will also rupture the H-H bond, possibly leading to metallic (conducting) behavior. The case at hand is clearly much more subtle. At the extreme pressures of the shock experiment, the H-H bond is significantly weakened, but even at $r_s = 1.5$ (~ 9 fold compression) the corresponding well depth continues to have a magnitude significantly larger than the temperatures achieved [61]. To date no evidence of static pressure induced dissociation in the solid has been observed, even at the significantly higher pressures of 250 GPa achieved by ultra pressure diamond anvil-cell techniques. Although the

evidence above refers to zero-temperature solids in particular structures, increasing the temperature is not likely to change the well depth significantly.

At these extremely high densities and temperatures, the very concept of *dissociation* is nebulous. High temperatures will excite large amplitude stretching motion, leading for example to exchange of atoms from neighboring pairs, or to the transient formation new localized species (“ H_3 ” etc...) and so standard chemical definitions are not unique. Perhaps it is better to speak of local coordination in a completely statistical sense, for example as the integral of the pair correlation function carried out to a certain distance. These changes in local coordination certainly lead to corresponding changes in the global electronic structure as pointed out in an interesting recent tight-binding (TB) molecular dynamics study by Lenosky et al. [62]. Here “dissociation” is defined by asserting that two atoms constitute a dimer if each forms the nearest neighbor atom of the other. Atoms not identified as belonging to a dimer are then termed dissociated “monomers”. Interestingly, they find that states near the chemical potential have a large projection onto these “monomers”, and so by virtue of the Mott formula, for which resistivity scales as the inverse square of the density of states at the Fermi energy, the resistivity in their simulation scales inversely with the square of the average number of “monomers”. The mechanism they propose (similar to that suggested by Ross [63]) in which the “dissociation” plays a crucial role is a possible candidate for what might happen in liquid metallic hydrogen. However the large Hubbard U , included only indirectly through the effective parameters in TB, suggests that dissociation does not necessarily imply a conducting state. This may help explain why the TB conductivities found at low density and pressure are much higher than the experimental ones [62].

Recently Pfaffenzeller and Hohl [64] carried out Car-Parrinello ab-initio molecular dynamics (AIMD) simulations on the metallic side of the M-I transition and find an even higher “dissociation fraction”. Because of the extremely short life-time of the pairs they term the metallic liquid “monatomic”, even though it retains significant pairing correlations. Their lowest density is slightly higher than the metallization density calculated for the experiments ($D_m = 0.4 \text{ mol/cm}^3$ vs. 0.32 mol/cm^3) and they find a resistivity about a factor 6 smaller than the experiments. Simulating the metal-insulator transition with AIMD is difficult because the local density approximation (LDA) underestimates the gap, and the sensitivity on k-point sampling [65] (the AIMD calculations above use only one k-point) makes accurate large-scale simulations computationally intensive. Once again, the large Hubbard U implies that spin correlations may be important, necessitating AIMD simulations based on spin density functional theory instead of the usual paramagnetic ansatz.

But whether any of these mechanisms describe the shock experiments [14] fully has yet to be established. The gap closes with increasing density even in an entirely diatomic phase, and if the TB or AIMD even slightly overestimate the “dissociation”, the metallization in the simulations will occur through the “dissociation mechanism” instead of through a pure band-overlap scenario. In fact, as evidenced from comparison of pair correlation functions, the TB and AIMD results give a larger “dissociation” fraction than the path-integral monte-carlo (PIMC) results of Magro *et al.* [66]. While PIMC includes the substantial zero-point motion of the protons which the TB and AIMD neglect, PIMC is usually carried out in a much smaller cell. Presently it is not clear which method is best suited to the experimental regime and the sensitive interdependence of dissociation and metallization physics coupled with a possible role for strong correlations will render an unambiguous interpretation of the simulations difficult.

Early predictions of finite-temperature pressure-induced metallization fall under the general rubric of *Plasma Phase Transitions* (PPT) [67]. Most theories take a chemical approach, that is the species (bound states) are well defined, and this is at variance with the extremely short life-times predicted by simulations. Besides ignoring the possibility of band-overlap metallization, the chemical models are typically based on pair-potentials and a free-rotation approximation, both of which are ill-defined at these densities as we have noted. The most comprehensive chemical model calculations were carried out by Saumon and Chabrier [68] who predict for the PPT a critical point at $T = 15310 \text{ K}$ and a density of $D_m = 0.18 \text{ mol/cm}^3$, and at higher densities and lower temperatures an increasingly discontinuous transition between a diatomic insulating state and an ionized (conducting) monatomic phase (see also Fig. (4)). In support of these chemical models, the physically based PIMC calculations [66] also give rather similar results. On the other hand the TB simulations give a gradual transition to a more “monatomic” phase. The metallization experiments appear just out of the range of the PPT predictions. To establish the existence of a PPT by shock experiments will also require a range of temperature and density data.

Clearly the experiments are in a very interesting regime; the interplay of thermal and electronic effects brings the system close to both the closing of the gap *and* the onset of pair fragmentation, the two being interconnected. Which occurs first will depend sensitively on the actual temperature and pressure and one could imagine different behaviors at different state points. For example at densities just below the proposed diatomic metal-insulator transition at 0 K one would expect a I-M transition of the band-overlap type while at higher temperature and lower densities structural change, if it exists, becomes more important. A definitive electronic interpretation of the Livermore shock experiments is still lacking, and could prove to be quite unlike the conventional explanations of transport properties of ordinary liquid metals.

X. FUTURE EXPERIMENTAL PROBES

Considerations based both on a simple band-overlap scenario within the Ziman formulation, and the “dissociation” based mechanism proposed by Ross and Lenosky *et al.* [62,63], predict that the conductivity is high, but that it should drop with increasing density. Experiments going to higher pressure would therefore be of great interest. However, so also would shock experiments at about the same compression but lower temperatures. If the arguments given above are valid, then as depicted in Fig. (4), a boundary should be crossed (at fixed P) locating the I-M transition. One could also envisage that at even higher pressures, the I-M transition would be at low enough temperature to be within reach of static pressure techniques such as diamond anvil cells [69].

The transition to a conducting state in hydrogen may be quite unusual. The tenacity with which H retains its pairing, an effect driven largely by exchange, can be manifested even in a metallic environment and at quite high temperatures. Though covalent, this ensuing state is not of a network character as in molten Si (or Ge), but a rapid exchange of pairs (akin to the fast exchange proceeding in Si and Ge) may be proceeding. It is an interesting and perhaps novel state of matter, which now merits considerable further study.

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$$S(\vec{k}, \omega) = \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \hat{\rho}(\vec{k}, t) \hat{\rho}^\dagger(\vec{k}, 0) \rangle$$
where $\hat{\rho}(k)$ is the one-particle density operator for protons) the resistivity is then given by:

$$\rho \sim \int_0^{2k_f} q^3 dq |v(q)|^2 \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} S(\vec{k}, \omega) \frac{\beta \hbar \omega}{(\exp(\beta \hbar \omega) - 1)}$$
which reduces to the usual Ziman formula for $k_B T \gg \hbar \omega$. The effect of the vibrations can be calculated and gives a correction to the static structure factor $S(q)$ proportional to q^2 , but with a small enough prefactor (the same order as the correction for finite ion mass) to be ignored at this level of approximation.
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- [48] The mean-free path is roughly given by: $l = [174a.u.] \times [(rs/a_0)^2 / \rho_\mu]$ [56], which implies a mean free path of about $9a.u.$ for a calculated resistivity of $\sim 50 \mu\Omega cm$. Thus the Ziman formalism is self-consistent in that sense. A lower effective carrier density raises rs , so that in this approach the mean free path is still greater than the inter-molecular spacing for the larger (experimental) resistivities.
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FIG. 1. **Schematic of electrical conductivity experiments on fluid metallic hydrogen.**

Four electrodes in (a) were connected to the circuit in (b). For conductivities lower than metallic, two probes were used. Trigger pins turn on the recording system. All cables are coaxial.

FIG. 2. **Effect of rise time on pressure-density states.**

(a) First pressure in hydrogen is $\sim P_f/30$, where P_f is incident shock pressure in Al_2O_3 . Successive reverberations comprise a quasi-isentrope up to pressure P_f . This quasi-isentrope is represented by ramp over $\sim 50ns$ from $P_f/30$ up to P_f . After reverberation is complete, P_f is held for $\sim 100ns$. If P_f were achieved in one jump, this state would be on single-shock Hugoniot. (b) Equation-of-state curves plotted as pressures versus density: 0 K isotherm, points reached by shock reverberations, and single-shock Hugoniot. Initial point is liquid H_2 at 1 atm.

FIG. 3. **Logarithm of electrical resistivity of H_2 and D_2 plotted versus pressure.**

The slope change at 140 GPa is identified as the transition from semiconducting to metallic fluid.

FIG. 4. **Schematic Phase Diagram**

The metal-insulator transition in the liquid occurs at considerably lower pressure than the predicted transition in the solid. We suggest a metal-insulator band starting from the zero-temperature solid, and increasing in temperature with decreasing density as depicted above. At very low temperatures it will be sharp with the character of a thermodynamic phase transition. At the other extreme of low density and very high temperatures, the metallization will be by gradual transformation to a temperature ionized plasma. At zero temperature the metal-insulator transition is predicted to occur before (at lower density than) the diatomic-atomic transition. What happens at higher temperatures remains to be established. Possibilities include the crossing or merging of the lines, as well as their termination in one or two critical points. Recent theoretical predictions of a Plasma Phase Transition (PPT) [66,68] are schematically depicted as well. Also depicted in the figure is the Simon equation for the melting line, and the orientationally disordered (I) and ordered phases (II) and (III) found in the solid [52]. We emphasize that this phase diagram is merely schematic; much still needs to be filled in.